



## Comparative study on electrochemical degradation of 2,4-dichlorophenol by different Pd/C gas-diffusion cathodes

Hui Wang<sup>a,b</sup>, Jianlong Wang<sup>b,\*</sup>

<sup>a</sup> College of Environmental Science and Engineering, Beijing Forestry University, Beijing 100083, PR China

<sup>b</sup> Laboratory of Environmental Technology, Institute of Nuclear and New Energy Technology, Tsinghua University, Beijing 100084, PR China

### ARTICLE INFO

#### Article history:

Received 9 September 2008

Received in revised form 2 December 2008

Accepted 6 December 2008

Available online 13 December 2008

#### Keywords:

Electrochemical oxidation

Gas-diffusion cathode

Pd/C catalyst

Chlorophenol

Priority pollutant

### ABSTRACT

Pd/C catalysts used for the Pd/C gas-diffusion cathodes were prepared by the hydrogen gas and/or formaldehyde reduction, and characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV). The electrochemical degradation of 2,4-dichlorophenol was investigated in a diaphragm electrolysis system, feeding with hydrogen gas then with air, using three different self-made gas-diffusion cathodes. The results indicated that the Pd/C gas-diffusion cathodes can not only reductively dechlorinate 2,4-dichlorophenols by feeding hydrogen gas, but also accelerate the two-electron reduction of oxygen ( $O_2$ ) to hydrogen peroxide ( $H_2O_2$ ) by feeding air. Therefore, both the removal efficiency and the dechlorination degree of 2,4-dichlorophenol all reached about 100% after 80 min by using Pd/C gas-diffusion cathode, which were better than that of the carbon/polytetrafluoroethylene (C/PTFE) gas-diffusion cathode (no catalyst). The Pd/C catalyst prepared by the hydrogen reduction method had higher stability and catalytic activity than that prepared by the formaldehyde reduction method. By high-performance liquid chromatogram (HPLC), the main intermediates of 2,4-dichlorophenol dechlorination in the cathodic compartment were identified as 4-chlorophenol and 2-chlorophenol, which could be further dechlorinated to form phenol. Hydroquinone was the first intermediate formed from the oxidation of phenol, which was subsequently dehydrogenated to benzoquinone. The further oxidation of benzoquinone, after benzene ring cleavage, led to the formation of aliphatic carboxylic acids such as maleic, fumaric, and oxalic acids.

© 2009 Elsevier B.V. All rights reserved.

## 1. Introduction

Chlorophenols are one kind of toxic organic compounds listed by the Environmental Protection Agency (EPA) as priority pollutants [1]. They are released into the environment mainly by the chlorination of municipal water, the degradation of some chemicals, and the manufacturing of various products such as pesticides, pharmaceuticals, and dyes. Examples include 2,4-dichlorophenol and 4-chlorophenol, which are used in large amounts in the production of pentachlorophenol (a wood preservative), 2,4-dichlorophenoxyacetic acid, and 2,4,5-trichlorophenoxyacetic acid (common herbicides). Strong resistance to physical, chemical, and biological treatments of chlorophenols causes hazardous influence on living organisms including human beings. As the accumulation of chlorinated aromatic compounds in the environment has become a serious problem nowadays, it is

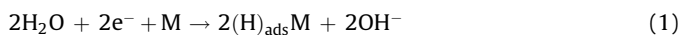
very urgent to develop an effective method to remove these contaminants.

It is well known that chlorinated compounds are toxic due to the chlorine contained in their structure. Traditional treatment processes such as biological treatments are not very effective for degradation of chlorinated phenols. Recently, advanced oxidation processes (AOPs) have attracted much attention, since they can be used to effectively treat wastewater containing chlorophenols. However, advanced oxidation processes usually open aromatic nucleus of chlorinated compounds and then form some chlorinated aliphatic intermediates [2]. The accumulation of chlorinated intermediates may be even more toxic than their parent compounds. The possibility to gain exhaustive dechlorination of chlorinated aromatic compounds by an electrochemical reductive approach was disclosed in the 1970s. This method ensured the selective removal of chlorine atoms from various chlorinated aromatic compounds under mild experimental conditions. However, such reported effective processes usually required non-aqueous reaction media or environmental unpleasant cathode materials (mercury or lead) [3–5], which made such methods unattractive for the possible practical application. The latter

\* Corresponding author. Tel.: +86 10 62784843; fax: +86 10 62771150.

E-mail address: [wangjl@mail.tsinghua.edu.cn](mailto:wangjl@mail.tsinghua.edu.cn) (J. Wang).

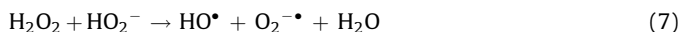
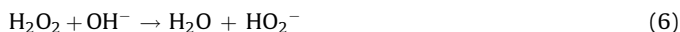
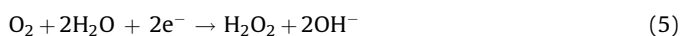
obstacle could be overcome by using carbon materials as the cathodes [6,7] while the suitable composition of reaction medium has been under consideration. The dechlorination of chlorinated aromatic compounds in aqueous medium was studied by using carbon materials loaded with Pd metals as cathodes [8–11]. According to the literature [12,13], the mechanism of the electrocatalytic hydrogenolysis of a carbon–chlorine bond involves the steps described in Eqs. (1)–(4), where M, (H)<sub>ads</sub>M and (R-Cl)<sub>ads</sub>M represent electrode surface, chemisorbed hydrogen and the adsorbed organic substrate, respectively.



Hydrogenolysis of the C–Cl bond was then catalytically processed by the reaction of adsorbed organic substrate with the chemisorbed hydrogen. Finally, the products desorbed from the surface of electrodes. However, most electrochemical reductive studies focus on the removal of chlorine atoms from the aromatic structure without further processes being applied simultaneously to treat the organic intermediates.

The electrochemical oxidation for the treatment of wastewater containing aromatic pollutants has attracted a great deal of attention recently, because of its ease of control, amenability to automation, high efficiency, and environmental compatibility [14]. At present, dimensionally stable anodes (DSA), which are typically prepared by thermal deposition of a thin layer of metal oxide (e.g., SnO<sub>2</sub>, PbO<sub>2</sub>, or IrO<sub>2</sub>) on a support metal, have been used for the oxidation of chlorophenol pollutants [15–21]. Usually, the electrochemical treatment can actualize the mineralization of organic pollutants by the stronger oxidant such as hydroxyl radicals (HO•), which are in situ generated by the electrochemical reaction on the electrode surface [22].

Very recently, indirect electro-oxidation methods for the wastewater treatment involving the H<sub>2</sub>O<sub>2</sub> electrogeneration have been developed. Carbon materials such as carbon/polytetrafluoroethylene (C/PTFE) [23–26], graphite [27,28], carbon felt [29,30] and reticulated vitreous carbon [31,32] are classified as electrode materials for the electrochemical production of H<sub>2</sub>O<sub>2</sub>. Generally, the electro-Fenton process can be realized in the undivided electrolytic cell, where H<sub>2</sub>O<sub>2</sub> is produced on the cathode and Fe<sup>2+</sup> is added in an acid medium [23–26,29–33]. As reported previously [34], we have explored a new electrochemical oxidation system to treat the aqueous organic pollutant without adding metal catalysts. It was performed in a diaphragm cell with a C/PTFE gas-diffusion cathode. In the diaphragm cell, where the terylene diaphragm was used, it could keep pH > 12 in the cathodic compartment and pH < 1 in the anodic compartment whether the original solution was acidic, neutral or alkaline. In the cathodic compartment (basic electrolyte) of the terylene diaphragm cell, C/PTFE O<sub>2</sub>-diffusion electrode catalyzes the two-electron reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> and HO<sub>2</sub><sup>•</sup>, which may be converted to HO• and O<sub>2</sub><sup>•-</sup> as follows [35]:



The degradation of organic pollutants was attributed to the cooperatively oxidation processes including direct and/or indirect electrochemical oxidations at the anode and by H<sub>2</sub>O<sub>2</sub>

and free radicals produced by the reduction of oxygen at the cathode.

In this paper, we report on the degradation of 2,4-dichlorophenol in a diaphragm cell with an organic synthesized diaphragm, a Ti/IrO<sub>2</sub>/RuO<sub>2</sub> anode, and self-made gas-diffusion cathodes. Pd/C catalyst used for the Pd/C gas-diffusion electrode was prepared and satisfactorily characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and cyclic voltammetry (CV). In addition, an effective and friendly method has been developed to treat contaminants of chloride compounds by using a combination process of reduction and oxidation. In the cathodic compartment, the chlorine atoms of chlorophenols were removed from the aromatic structure and chlorophenols were reduced to non-chloride intermediates. Then, the non-chloride intermediates were oxidized and degraded in the anodic and cathodic compartments. Main intermediates during the degradation of 2,4-dichlorophenol have been identified by chromatographic technique. Finally, the electrochemical degradation of 2,4-dichlorophenol by using the Pd/C gas-diffusion electrode as a cathode was compared to that by using the C/PTFE gas-diffusion cathode.

## 2. Experimental

### 2.1. Preparation of Pd/C catalyst and gas-diffusion cathode

Pd/C catalyst was prepared by hydrogen gas reduction and the formaldehyde reduction, respectively. Activated carbon powder was used as a catalyst support, and nitric acid treatment was carried out by heating an appropriate amount of activated carbon in a 10% nitric acid solution at reflux for 2 h. After that, the sample was washed with distilled water until neutrality and then dried overnight at 100 °C. Palladium chloride was firstly dissolved in a concentrated hydrochloric acid solution and then diluted with 15 mL of water. The solution of PdCl<sub>2</sub> was dropped into a vigorously stirred activated carbon solution at 80 °C. Pd/C catalyst prepared by hydrogen gas reduction (Pd<sub>H</sub>/C catalyst): the mixture was kept at 80 °C for 2 h and then was evaporated to dryness. The dried catalyst was further reduced at 250 °C in a stream of hydrogen gas with a rate of 30 mL min<sup>-1</sup> for 2 h, and then cooled to ambient temperature under a hydrogen atmosphere. Finally, Pd<sub>H</sub>/C catalyst with a Pd load of 0.5 wt.% was obtained and stored in a desiccator. Pd/C catalyst prepared by formaldehyde reduction (Pd<sub>F</sub>/C catalyst): the mixture was kept at 80 °C for 2 h and then was cooled to 40 °C. A 36% formaldehyde solution was added to the vigorously stirred mixture. After the addition, stirring was kept for 30 min, a 30% NaOH solution was then added dropwise in order to take the mixture pH at 8–9. The formed catalyst was then washed six times by decanting with water. After being filtered on a sintered crucible, washed and dried, Pd<sub>F</sub>/C catalyst with a Pd load of 0.5 wt.% was obtained. The gas-diffusion cathodes were prepared according to the reported procedure [36].

### 2.2. Procedures

Electrolysis was conducted in a terylene diaphragm cell of 100 mL with a Ti/IrO<sub>2</sub>/RuO<sub>2</sub> anode (16 cm<sup>2</sup>) and a gas-diffusion cathode (16 cm<sup>2</sup>). A schematic diagram of the experimental setup has been described elsewhere [37]. A laboratory direct current power supply with current–voltage monitor was employed to provide the electric power. The synthetic wastewater was used. The experimental conditions were as follows: the initial 2,4-dichlorophenol concentration was 100 mg L<sup>-1</sup>; the current density was 39 mA cm<sup>-2</sup>; the concentration of supporting electrolyte (Na<sub>2</sub>SO<sub>4</sub>) was 0.1 mol L<sup>-1</sup>; the distance between electrodes was 2 cm; the initial pH was 7.0. Before starting electrolysis, hydrogen

gas was fed for 5 min with the rate of feeding gas was  $25 \text{ mL s}^{-1}$  in order to keep dissolved gas saturation. Hydrogen gas was then fed into the gas compartment during 0–80 min (electrolysis time), following air.

### 2.3. Analytical methods

The XRD patterns were used to identify any present phase and their crystallite size. The Pd/C catalyst was characterized by XRD with a Rigaku D/max-III A X-ray power diffractometer using Cu K $\alpha$  radiation with a Ni filter. In addition, the Pd particle morphology and size distributions were determined by TEM: JEM-2010F TEM microscope operated at an accelerating voltage of 200 kV. The surface composition of catalyst and Pd surface concentration was then investigated by XPS on PHI5300 Electron Spectrometer (Mg K $\alpha$  radiation;  $h\nu = 1253.6 \text{ eV}$ ). XPS data were calibrated using the binding energy of C1s (284.6 eV) as the standard.

The CV spectra were recorded using a potentiostat/galvanostat (EG&G Model 273A) with a standard three-compartment cell consisting of a Pt wire as a counter electrode, an Ag/AgCl electrode as a reference, and the Pd/C catalyst (or activated carbon) modified electrode as a working electrode. The Pd/C catalyst (or activated carbon) modified electrode was prepared as follows: 5 mg of Pd/C catalyst (or activated carbon) was suspended in a mixture of 1 mL of ethanol and 50  $\mu\text{L}$  of Nafion<sup>®</sup> solution (5 wt.% Aldrich solution) to prepare a catalyst ink. Then 10  $\mu\text{L}$  of ink was transferred with an injector to the surface of a clean glassy carbon disk electrode (with area of  $0.126 \text{ cm}^2$ ). After the ethanol evaporated, the electrode was heated at  $75^\circ\text{C}$  for 10 min.  $0.5 \text{ mol L}^{-1}$  of  $\text{Na}_2\text{SO}_4$  solution was used as an electrolyte, which was saturated with oxygen by feeding oxygen gas throughout the electrolysis. During the experiment process, the electrolyte temperature was kept constant at  $25^\circ\text{C}$ . The scan rate was  $100 \text{ mV s}^{-1}$ .

The determination of 2,4-dichlorophenol and its stable degradation products in electrolyzed solutions were carried out using high-performance liquid chromatogram (HPLC, Shimadzu, Japan) analyses by comparing the retention time with those of the standard compounds. Samples of 20  $\mu\text{L}$  previously filtered with PTFE filters of  $0.45 \mu\text{m}$  were injected to the HPLC. The separation was performed using a Zentris ODS-SP C18 column ( $250 \text{ mm} \times 4.6 \text{ mm}$ ,  $5 \mu\text{m}$ ) at a flow rate of  $1.0 \text{ mL min}^{-1}$  and at column temperature of  $25^\circ\text{C}$ . The aromatic compounds were determined by HPLC, running with mobile phase of methanol/water (v/v) at 80/20, and an UV detector was set at a wavelength of 280 nm, except for benzoquinone, whose concentration was

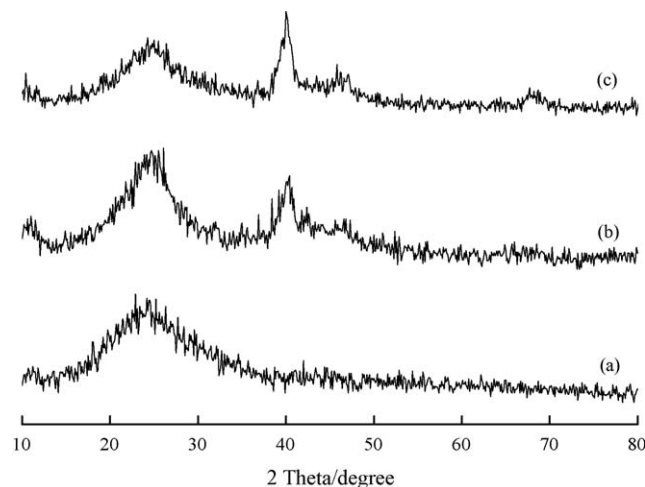


Fig. 1. XRD pattern of activated carbon (a), Pd<sub>H</sub>/C catalyst (b) and Pd<sub>F</sub>/C catalyst (c).

measured at 254 nm. The carboxylic acids were determined by HPLC, running with mobile phase of methanol/ $\text{KH}_2\text{PO}_4$  25/75 (v/v) at pH 2.1 adjusted with  $\text{H}_3\text{PO}_4$ , and an UV detector (210 nm) was employed.

The total organic carbon (TOC) was detected by an Elemental High TOC analyzer. The concentration of chloride ion in electrolyzed solutions was determined by titration with mercury nitrate using a standard procedure.

## 3. Results and discussion

### 3.1. Characterization of Pd/C catalyst

The XRD patterns of catalysts are shown in Fig. 1. The characteristic diffraction peak of a Pd particle is found at about  $40.6^\circ$  which indicate the catalyst reduced by hydrogen gas and formaldehyde [38]. With the diameter of Pd particles increasing, the Pd peak became narrower and sharper. There are no other distinct reflection peaks in the spectra other than the peak mentioned above, indicating that the home-made Pd/C catalyst had prevailed Pd structure. These observations suggested that the Pd particles were amorphous less than 4.0 nm and highly dispersed over the activated carbon supports.

In order to estimate the geometry and the particle size of the Pd species, TEM image of Pd/C catalyst and its metal particle

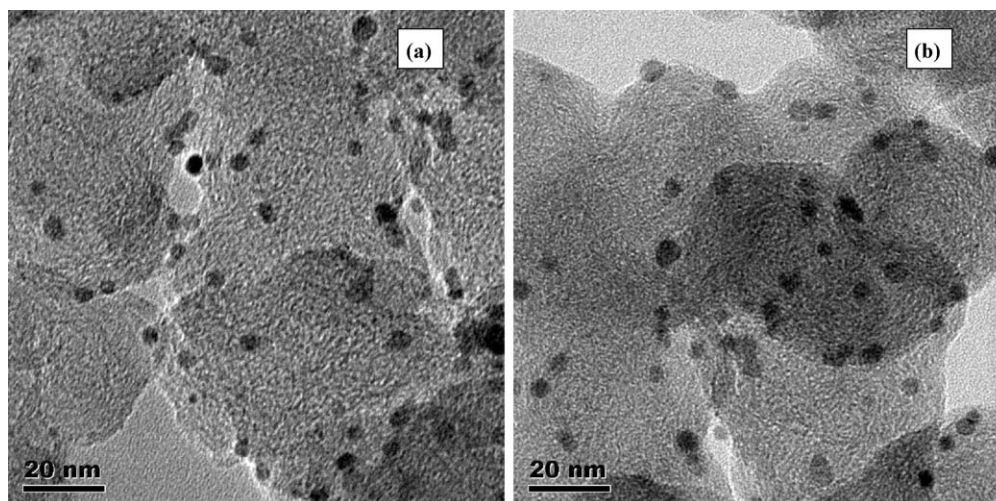


Fig. 2. TEM pattern of Pd<sub>H</sub>/C catalyst (a) and Pd<sub>F</sub>/C catalyst (b).



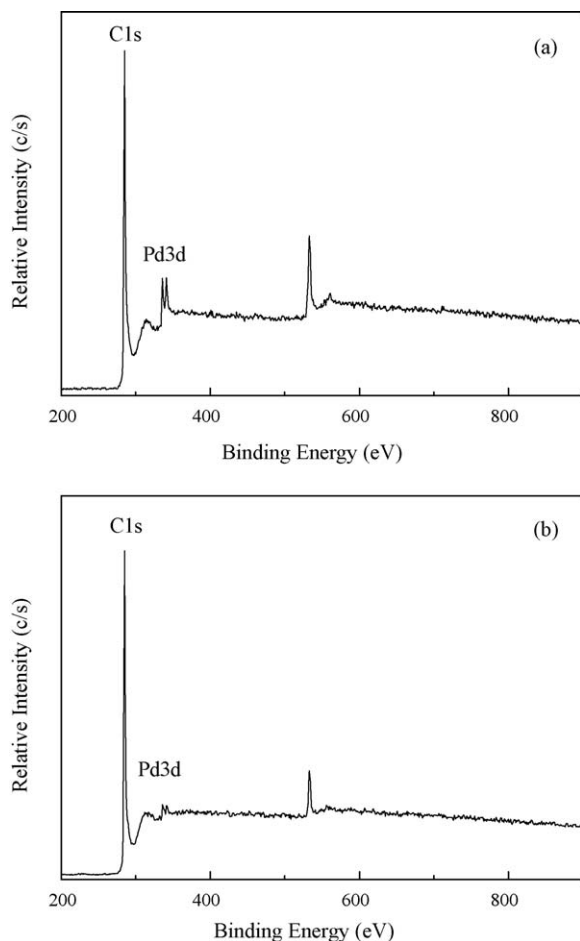


Fig. 3. XPS pattern of Pd<sub>H</sub>/C catalyst (a) and Pd<sub>F</sub>/C catalyst (b).

size distribution was measured (Fig. 2). It clearly shows Pd species, as spherical and half-spherical grains, are homogeneously dispersed on the supports. Pd/C catalyst was characterized by a narrow distribution of smaller Pd particles to give a surface area weighted mean particle diameter. The mean particle size of Pd<sub>H</sub>/C catalyst was higher than that of Pd<sub>F</sub>/C catalyst. The samples of Pd<sub>H</sub>/C catalyst and Pd<sub>F</sub>/C catalyst had mean size of 4.1 and 5.2 nm, respectively, which were smaller than the previous observations [39]. The values of the mean particle size obtained by TEM analysis were in good agreement with those calculated from the XRD results.

Chemical states of surface atoms in the catalysts were investigated by XPS (Fig. 3). It can be seen that the binding energies of Pd<sub>3d</sub> in the reduced catalyst are 335.1 and 336.2 eV, which are almost similar to the data in the previous observations [40] which could be assigned to Pd and Pd (II), respectively. Pd particles content on the surface of Pd<sub>H</sub>/C catalyst reached 1.3 at.%, higher than that of Pd<sub>F</sub>/C catalyst.

Fig. 4 gives CV curves. There is intense reduction peak at about  $-0.30$  V in the presence of oxygen in a basic solution. It indicates that the two-electron reduction of O<sub>2</sub> to peroxide anion (HO<sub>2</sub><sup>−</sup>) led the formation of reduction current peaks using catalyst modified electrodes. The reduction current peak of the Pd/C catalyst modified electrode is higher than that of the no catalyst modified electrode. This can be attributed to that Pd/C catalyst accelerates the two-electron reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. Furthermore, Pd<sub>H</sub>/C catalyst showed higher activity to oxygen reduction than Pd<sub>F</sub>/C catalyst.

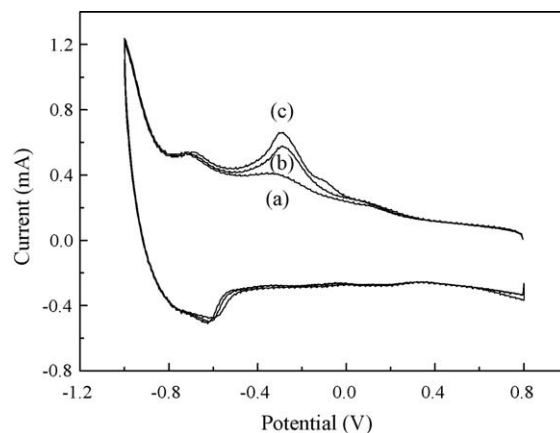


Fig. 4. CV curves for activated carbon (a), Pd<sub>F</sub>/C catalyst (b) and Pd<sub>H</sub>/C catalyst (c) at oxygen gas.

### 3.2. Removal and dechlorination degree of 2,4-dichlorophenol

Fig. 5 shows the removal efficiency of 2,4-chlorophenol and variation of TOC with electrolysis time in the cathodic and anodic compartments using three different gas-diffusion electrode systems, respectively.

As shown in Fig. 5a, in the initial 80 min, the removal efficiency of 2,4-dichlorophenol increased with electrolysis time in the cathodic compartment using three different gas-diffusion electro-

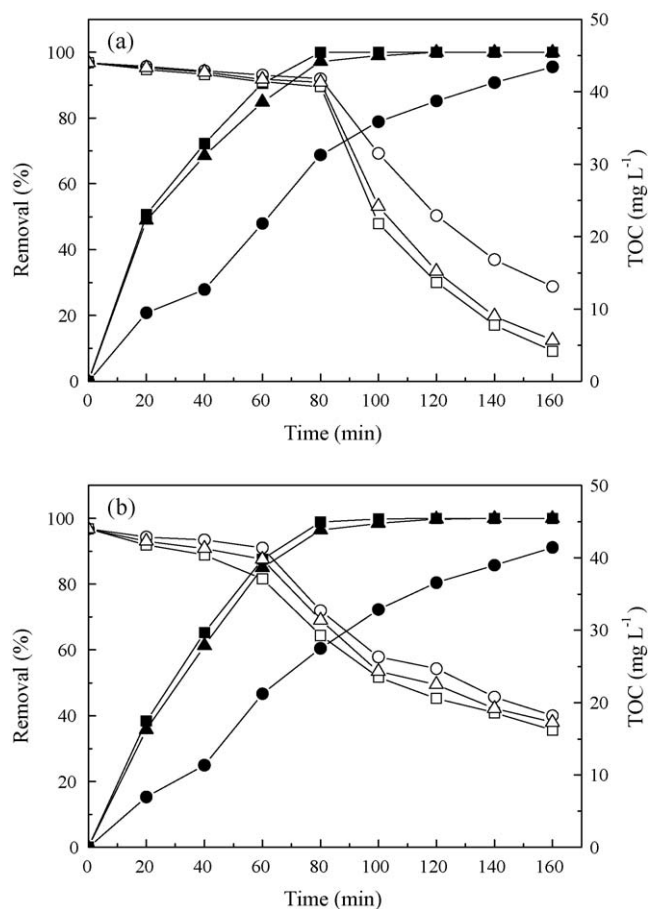


Fig. 5. Removal of 2,4-dichlorophenol (●, ■, and ▲) and variation of TOC (○, □, and △) in the cathodic compartment (a) and anodic compartment (b) with electrolysis time at feeding hydrogen and air by the C/PTFE (● and ○), Pd<sub>H</sub>/C (■ and □) and Pd<sub>F</sub>/C (▲ and △) gas-diffusion electrode system. [2,4-dichlorophenol]<sub>0</sub> = 100 mg L<sup>−1</sup>.

des by feeding hydrogen gas. This trend could be attributed to the fact that hydrogen atom is a powerful reducing agent which reductively dechlorinates chlorophenols, which is in favor of improving the removal efficiency of 2,4-dichlorophenols. Palladium is not only a catalyst for the hydrogen evolution but also a facilitator for the reductive dechlorination of organic compounds. The high reactivity of the Pd/C gas-diffusion electrode system can be attributed to the following sequence of reactions [8]: (1) the evolution of hydrogen gas by the reduction of water; (2) the adsorption of evolved hydrogen gas by Pd, and then formation of a powerful reducing species,  $\text{Pd}^*\text{H}_2$ ; (3) the reduction of chlorinated organic compounds adsorbed on the surface of Pd/C gas-diffusion electrodes. Therefore, the removal efficiency of 2,4-dichlorophenol reached about 100% at 80 min by using  $\text{Pd}_{\text{H}}/\text{C}$  and  $\text{Pd}_{\text{F}}/\text{C}$  gas-diffusion electrode systems, was higher than that of C/PTFE gas-diffusion electrode system by feeding hydrogen gas. The removal efficiency for 2,4-dichlorophenol used  $\text{Pd}_{\text{H}}/\text{C}$  gas-diffusion cathode is slightly higher than that of  $\text{Pd}_{\text{H}}/\text{C}$  gas-diffusion cathode in the cathodic compartment (see Fig. 5a). It indicates that the activity of  $\text{Pd}_{\text{H}}/\text{C}$  catalyst is higher than that of  $\text{Pd}_{\text{F}}/\text{C}$  catalyst which also conformed by the XRD, TEM and XPS results.

However, in the initial 80 min, TOC removal of the cathodic compartment increased slightly with prolonged the electrolysis time in three systems. After 80 min, feeding air was used instead of feeding hydrogen gas, and TOC removal of the cathodic compartment markedly increased (see Fig. 5a). In the initial 80 min, it was believed that the non-chloride intermediates were not be further oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  in the cathodic compartment, which did not produce  $\text{H}_2\text{O}_2$  by the electro-reduction of dissolved oxygen during feeding hydrogen gas. After 80 min, it was obviously that gas-diffusion electrode catalyzed the two-electron reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$  and  $\text{HO}_2^-$ , which may be converted to  $\text{HO}^\bullet$  and  $\text{O}_2^{\bullet-}$  by feeding air. TOC removal of the Pd/C gas-diffusion electrode system was higher than that of C/PTFE gas-diffusion electrode system in the cathodic compartment (see Fig. 5a). This can be attributed to that Pd/C catalyst in Pd/C gas-diffusion electrode system accelerated the two-electron reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}_2$  when feeding air, which was consistent with CV conclusions.

The changing trend of removal efficiency of 2,4-chlorophenol in the anodic compartment is similar with that in the cathodic compartment in three different kinds of gas-diffusion electrode systems (see Fig. 5b). However, the removal efficiency of 2,4-dichlorophenol and TOC removal in the anodic compartment was lower than that in the cathodic compartment in the same system. Although the degradation of 2,4-dichlorophenol in the anodic compartment was supposed to the oxidation of  $\text{MO}_x(\text{OH}^\bullet)$  or  $\text{MO}_{x+1}$  produced on the anode surface [41], the anodic oxidation was difficult to achieve total mineralization because of low  $\text{MO}_x(\text{OH}^\bullet)$  or  $\text{MO}_{x+1}$  concentration on the anode.

The concentration of chloride ion released from the selected aromatic compounds by electrochemical oxidation was measured to evaluate the dechlorination degree. Chloride substituents are usually responsible to the toxicity of aromatic compounds. Therefore, the dechlorination degree indirectly represented the detoxification degree. In three systems, the changes of the concentration of chloride ion with electrolysis time in the cathodic and anodic compartments are illustrated in Fig. 6. The changing trends of the chloride ion concentration in the anodic and cathodic compartments were similar in three systems. With an increasing of electrolysis time (0–80 min), the concentration of chloride ion increased in both anodic and cathodic compartments, however, the concentration of chloride ion in the anodic compartment was higher than that in the cathodic compartment in the same system. This trend was attributed to that in the initial electrolysis period, many formed chloride ions in a cathodic compartment diffused to an anodic compartment through a terylene diaphragm due to the electro-

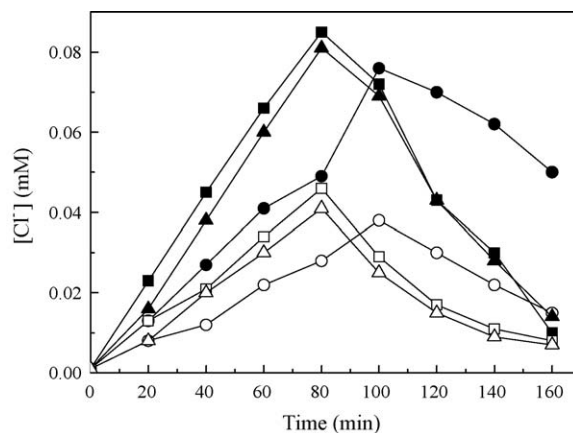


Fig. 6. Variation of  $\text{Cl}^-$  concentration in the cathodic compartment ( $\circ$ ,  $\square$ , and  $\triangle$ ) and anodic compartment ( $\bullet$ ,  $\blacksquare$ , and  $\blacktriangle$ ) with electrolysis time at feeding hydrogen and air by the C/PTFE gas-diffusion electrode system ( $\bullet$  and  $\circ$ ); the  $\text{Pd}_{\text{H}}/\text{C}$  gas-diffusion electrode system ( $\blacksquare$  and  $\square$ ); the  $\text{Pd}_{\text{F}}/\text{C}$  gas-diffusion electrode system ( $\blacktriangle$  and  $\triangle$ ).  $[\text{2,4-dichlorophenol}]_0 = 100 \text{ mg L}^{-1}$ .

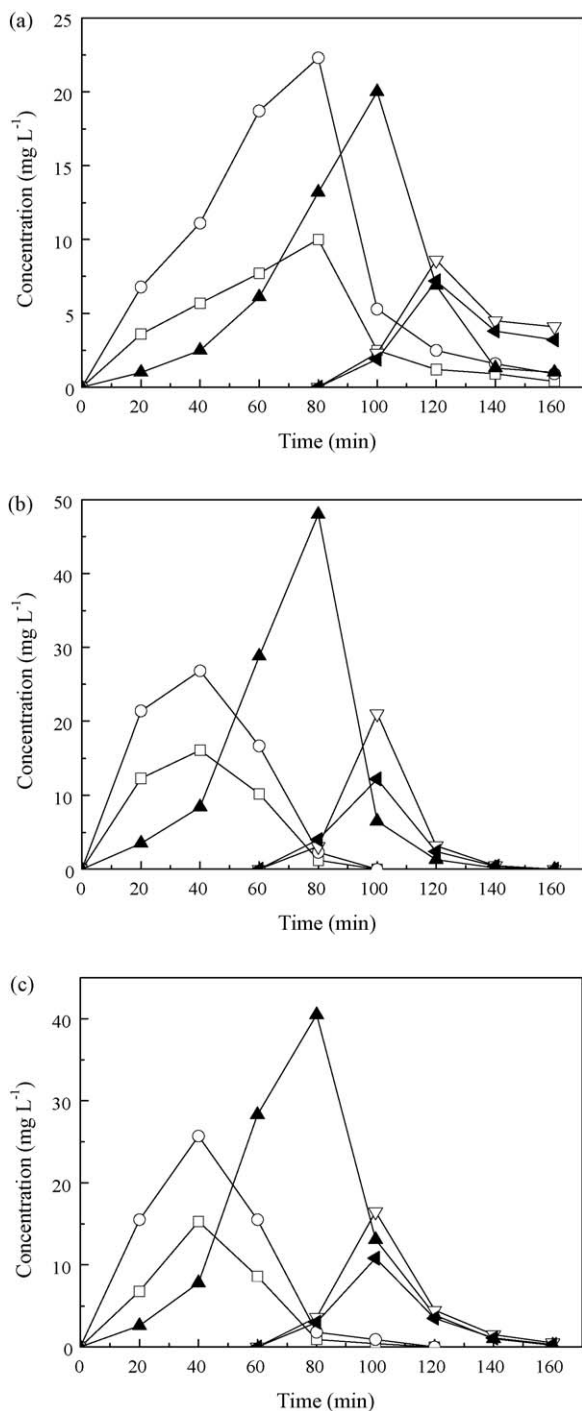
static repulsion from a negatively charged cathode. Therefore, the concentrations of chloride ion in anodic compartments were high. With the increase of electrolysis time, the concentration of chloride ion reached the highest value and then decreased in both compartments. Results indicated that chloride ion was oxidized to  $\text{Cl}_2$  gas which immediately release at the anode, as reported in the electrolysis of chlorophene with BDD anode [42].

The concentration of the chloride ion in Pd/C gas-diffusion cathode system reached its climate earlier than that in C/PTFE gas-diffusion cathode system (the former was 80 min and the latter was 100 min). After 80 min, the release of chloride ions is quantitative in the  $\text{Pd}_{\text{H}}/\text{C}$  gas-diffusion electrode system (see Fig. 6). This can be attributed to that Pd promotes the cleavage of carbon–chlorine bonds and facilitates hydrogenation by feeding hydrogen gas. Therefore, it is feasible to degrade chlorinated contaminants by electrochemical reduction to non-chlorinated intermediates in the Pd/C gas-diffusion electrode system.

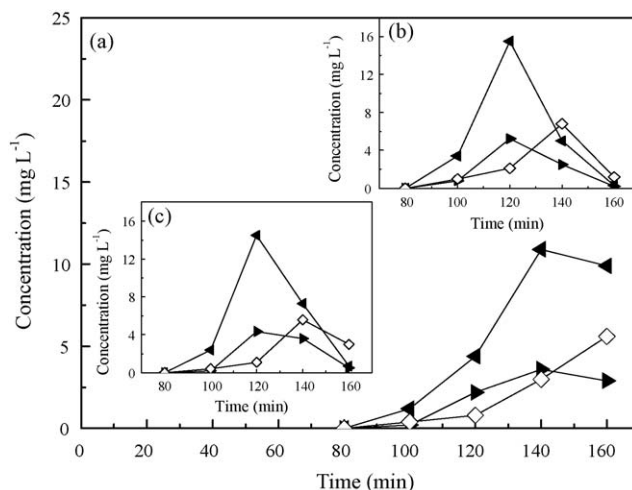
### 3.3. Identification of intermediates and their evolution

It is noteworthy that the dechlorination of 2,4-dichlorophenol could form monochlorophenols and phenol [7,43]. Additionally, the electrochemical degradation of aromatic compounds leads to a mixture of carboxylic acids [44]. According to the classical 2,4-dichlorophenol reduction and phenol oxidation scheme proposed in Refs. [7,43,44], a  $100 \text{ mg L}^{-1}$  2,4-dichlorophenol solution was electrolyzed for 160 min by three different gas-diffusion electrode systems to try to ascertain the stable intermediates formed by HPLC. The stable aromatic intermediates were analyzed using an 80/20 (v/v) methanol/water mixture as mobile phase at  $1.0 \text{ mL min}^{-1}$  and at  $25^\circ\text{C}$ . The chromatograms exhibit peaks corresponding to 4-chlorophenol, 2-chlorophenol, phenol, hydroquinone, and benzoquinone at the retention time of 4.46, 4.15, 3.82, 2.32 and 3.66 min, respectively. All these aromatics were unequivocally identified by comparing their retention times and UV–vis spectra, measured on the UV detector (280 nm, except for benzoquinone, whose concentration was measured at 254 nm), with those of authentic compounds. The HPLC data of the same electrolyzed solutions, using a 25/75 (v/v) methanol +  $\text{KH}_2\text{PO}_4$  (pH 2.1) as eluent at  $1.0 \text{ mL min}^{-1}$  and an UV detector (210 nm), displayed different peaks related to short carboxylic acids such as maleic, fumaric, crylic, malonic, oxalic, acetic, and formic at the retention time of 3.73, 5.09, 6.59, 3.34, 2.68, 4.23 and 3.02 min, respectively. The analyses showed the main intermediates were 4-chlorophenol, 2-chlorophenol, phenol, hydroquinone, benzoquinone, maleic, fumaric and oxalic acids. In

addition, acrylic, malonic, acetic and formic acids were detected in trace amounts. These intermediates are similar with several studies conducted using other electrochemical oxidation techniques [45,46]. No other possible intermediates were detected. In order to contrast the goodness of the analytically determined composition, TOC estimation were compared with experimental TOC resulting in deviations less than 5%, indicating that the carbon mass balance is very reasonably closed. Figs. 7 and 8 show the evolution of the concentration of all aromatic intermediates and selected carboxylic



**Fig. 7.** Evolution of the concentration of aromatic intermediates in the cathodic compartment: 4-chlorophenol (□), 2-chlorophenol (○), phenol (▲), hydroquinone (◄), and benzoquinone (▽) during the degradation of 2,4-dichlorophenol with electrolysis time at feeding hydrogen and air by the C/PTFE gas-diffusion electrode system (a); the Pd<sub>H</sub>/C gas-diffusion electrode system (b); the Pd/C gas-diffusion electrode system (c). [2,4-dichlorophenol]<sub>0</sub> = 100 mg L<sup>-1</sup>.



**Fig. 8.** Variation of the concentration of selected carboxylic acids in the cathodic compartment: maleic acid (◄), fumaric acid (►), and oxalic acid (◇) during the degradation of 2,4-dichlorophenol with electrolysis time at feeding hydrogen and air by the C/PTFE gas-diffusion electrode system (a); the Pd<sub>H</sub>/C gas-diffusion electrode system (b); the Pd/C gas-diffusion electrode system (c). [2,4-dichlorophenol]<sub>0</sub> = 100 mg L<sup>-1</sup>.

acids during the degradation of 2,4-dichlorophenol by three different gas-diffusion electrode systems, respectively. A fast formation and destruction of main intermediates can be observed.

4-Chlorophenol, 2-chlorophenol and phenol are the main dechlorination products in electrolysis (0–80 min) feeding hydrogen gas in three different gas-diffusion electrode systems (see Fig. 7). After 80 min, the main oxidized products were hydroquinone, benzoquinone, maleic acid, fumaric acid, and oxalic acid (see Figs. 7 and 8). The concentration of dechlorination products (4-chlorophenol and 2-chlorophenol) increased in the first 80 min and then decreased till complete removal within 160 min (see Fig. 7a). Additionally, the amount of 2-chlorophenol was more than that of 4-chlorophenol in the solution during the electrolysis. That is attributed to the facts that the reactivity of Cl at 4-position of 2,4-dichloroaromatics was higher than of Cl at 2-position due to the steric hindrance caused by the neighbouring functional groups, as it was suggested earlier for 2,4-D [7]. Furthermore, reductive cleavage of C–Cl bond at 4-position of the phenyl ring proceeded faster than that at 2-position.

The results of HPLC analyses of electrolysis solutions in the Pd<sub>H</sub>/C gas-diffusion electrode system are shown in Figs. 7b and 8b. The dechlorination products (4-chlorophenol, 2-chlorophenol, and phenol) and oxidation intermediates (hydroquinone, benzoquinone, maleic acid, fumaric acid, and oxalic acid) were found at a larger amount and in shorter period in the Pd<sub>H</sub>/C gas-diffusion electrode system than that in the C/PTFE gas-diffusion electrode system by feeding firstly with hydrogen gas followed by air. For example, a great accumulation of phenol up to 48.0 mg L<sup>-1</sup> at 80 min of electrolysis in the Pd<sub>H</sub>/C gas-diffusion electrode system and its complete mineralization in 140 min are observed (see Fig. 7b), whereas for the C/PTFE gas-diffusion electrode system (see Fig. 7a), phenol persists for 160 min, reaching 20.0 mg L<sup>-1</sup> as maximum in 100 min. After 80 min no traces of chlorinated aromatic compounds can be detected, and after 160 min most of aliphatic carboxylic acids were transformed into carbon dioxide and water in the Pd<sub>H</sub>/C gas-diffusion electrode system (see Figs. 5a, 7b and 8b). Whereas, a little chlorinated aromatic compounds and most of aliphatic carboxylic acids are presented after 160 min in the C/PTFE gas-diffusion electrode system (see Figs. 5a, 7a and 8a). These results clearly demonstrated that 2,4-dichlorophenol was

effectively dechlorinated and its intermediates were rapidly oxidized while Pd<sub>H</sub>/C catalyst was used in the gas diffuse cathode. Therefore, Pd played an important role in the degradation of 2,4-dichlorophenol. The Pd<sub>H</sub>/C gas-diffusion cathode can not only reductively dechlorinate 4-chlorophenols by feeding hydrogen gas, but also accelerate the two-electron reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> by feeding air, which is consistent with CV conclusions (see Fig. 4). Similar results were found for the same intermediates in the Pd<sub>F</sub>/C gas-diffusion electrode system. However, the amounts of them were lower than that of the Pd<sub>H</sub>/C gas-diffusion electrode system (see Figs. 7b and c and 8c).

The degradation pathway in the anodic compartment of three kinds of gas-diffusion electrode systems was proposed as follows: 2,4-dichlorophenol was dechlorinated to 4-chlorophenol and 2-chlorophenol, which were then converted to phenol by losing chlorine atoms. Hydroquinone was the first product after the oxidation of phenol, which was subsequently dehydrogenated to benzoquinone. The continually oxidation of benzoquinone, after ring opening, then led to the formation of aliphatic carboxylic acids such as maleic, fumaric, and oxalic acids. Finally, the terminal products were carbon dioxide and water. Through HPLC analyses, the main intermediates were chlorocatechol, hydroquinone, benzoquinone, and aliphatic carboxylic acids in the anodic compartment of three kinds of gas-diffusion electrode systems. The aliphatic carboxylic acids were the main intermediates after 120 min. Therefore, the principal reaction had been turned to the mineralization of aliphatic carboxylic acids to CO<sub>2</sub> after 120 min in the Pd<sub>H</sub>/C gas-diffusion electrode system. Owing to its low current efficiency, in practical use, it was not necessary to degrade 2,4-dichlorophenol to the final products, CO<sub>2</sub>. It may be more worthwhile to degrade 2,4-dichlorophenol to the biodegradable stage-aliphatic carboxylic acids which could then be economical treated by biological process.

#### 4. Conclusions

Three different Pd/C gas-diffusion cathodes were prepared and investigated for degrading 2,4-dichlorophenol in an aqueous solution. In the Pd<sub>H</sub>/C catalyst, Pd particles of an average size of 4.1 nm were highly dispersed in activated carbon with amorphous structure; the Pd content on the surface of Pd/C catalyst was 1.3 at.%. The Pd/C gas-diffusion cathodes can not only reductively dechlorinate 2,4-dichlorophenols by feeding hydrogen gas, but also accelerate the two-electron reduction of O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub> by feeding air. Hence, the removal efficiency of 2,4-dichlorophenol by using the Pd/C gas-diffusion cathode was better than that of the C/PTFE gas-diffusion cathode. In addition, the activity of Pd<sub>H</sub>/C catalyst was higher than that of Pd<sub>F</sub>/C catalyst. In the Pd<sub>H</sub>/C gas-diffusion electrode system feeding with hydrogen gas then with air, both the removal efficiency and the dechlorination degree of 4-chlorophenol reached about 100% after 80 min. Compared with the C/PTFE gas-diffusion electrode system, the Pd<sub>H</sub>/C gas-diffusion electrode system converted 2,4-dichlorophenols to the dechlorinated intermediates (4-chlorophenol, 2-chlorophenol, and phenol) and oxidized products (hydroquinone, benzoquinone, maleic acid, fumaric acid, and oxalic acid) in a shorter electrolysis time.

#### Acknowledgements

This work was supported by the National Natural Science Foundation of China (Grant Nos. 50325824 and 50678089), the Chinese Postdoc Fund (Grant No. 20060390454) and the Excellent Young Teacher Program of MOE, P.R. China, which are greatly acknowledged.

#### References

- [1] C.H. Lin, S.K. Tseng, *Chemosphere* 39 (1999) 2375–2389.
- [2] A. Hirvonen, M. Trapido, J. Hentunen, J. Tarhanen, *Chemosphere* 41 (2000) 1211–1218.
- [3] P.R. Birkin, A. Evans, C. Milhano, M.I. Montengro, D. Pletcher, *Electroanalysis* 16 (2004) 583–587.
- [4] T.F. Connors, J.F. Rusling, *J. Electrochem. Soc.* 130 (1983) 1120–1121.
- [5] S.G. Merica, N.J. Bunce, W. Jedral, J. Lipkowski, *J. Appl. Electrochem.* 28 (1998) 645–651.
- [6] G. Chen, Z.Y. Wang, D.G. Xia, *Electrochim. Acta* 50 (2004) 933–937.
- [7] A.I. Tsyganok, I. Yamanaka, K. Otsuka, *Chemosphere* 39 (1999) 1819–1831.
- [8] I.F. Cheng, Q. Fernando, N. Korte, *Environ. Sci. Technol.* 31 (1997) 1074–1078.
- [9] A.I. Tsyganok, K. Otsuka, *Appl. Catal. B: Environ.* 22 (1999) 15–26.
- [10] L. Calvo, M.A. Gilarranz, J.A. Casas, A.F. Mohedano, J.J. Rodriguez, *Appl. Catal. B: Environ.* 67 (2006) 68–76.
- [11] Y.X. Fang, S.R. Al-Abed, *Appl. Catal. B: Environ.* 80 (2008) 327–334.
- [12] P. Dabo, A. Cyr, F. Laplante, F. Jean, H. Menard, J. Lessard, *Environ. Sci. Technol.* 34 (2000) 1265–1268.
- [13] C.Y. Cui, X. Quan, H.T. Yu, Y.H. Han, *Appl. Catal. B: Environ.* 80 (2008) 122–128.
- [14] Ch. Comninellis, *Electrochim. Acta* 39 (1994) 1857–1862.
- [15] U. Leffrang, K. Ebert, K. Flory, *Sep. Sci. Technol.* 30 (1995) 1883–1889.
- [16] A.M. Polcaro, S. Palmas, F. Renoldi, M. Mascia, *J. Appl. Electrochem.* 29 (1999) 147–151.
- [17] A.M. Polcaro, S. Palmas, F. Renoldi, M. Mascia, *Electrochim. Acta* 46 (2000) 389–394.
- [18] J.D. Rodgers, W. Jedral, N.J. Bunce, *Environ. Sci. Technol.* 33 (1999) 1453–1457.
- [19] B.J. Hwang, K.L. Lee, *J. Appl. Electrochem.* 26 (1996) 153–159.
- [20] O.A. Mohammed, A.T. Mousa, T. Yahya, *J. Hazard. Mater.* B75 (2000) 99–113.
- [21] C.L. Zanta, P.A. Michaud, Ch. Comninellis, A.R. De, *J. Appl. Electrochem.* 33 (2003) 1211–1215.
- [22] J.E. Vitt, D.C. Johnson, *J. Electrochem. Soc.* 139 (1992) 774–780.
- [23] T. Harrington, D. Pletcher, *J. Electrochem. Soc.* 146 (1999) 2983–2989.
- [24] E. Brillas, R. Saulea, J. Casado, *J. Electrochem. Soc.* 145 (1998) 759–765.
- [25] E. Brillas, B. Boye, I. Sires, *Electrochim. Acta* 49 (2004) 4487–4496.
- [26] E. Brillas, E. Mur, J. Casado, *J. Electrochem. Soc.* 143 (1996) L49–L53.
- [27] J.S. Do, C.P. Chen, *J. Appl. Electrochem.* 24 (1994) 936–942.
- [28] K.B. Lee, M.B. Gu, S.H. Moon, *Water Res.* 37 (2003) 983–992.
- [29] M.A. Oturan, E. Guivarch, N. Oturan, I. Sirés, *Appl. Catal. B: Environ.* 82 (2008) 244–254.
- [30] M.A. Oturan, N. Oturan, C. Lahitte, S. Trevin, *J. Electroanal. Chem.* 507 (2001) 96–102.
- [31] C.P. Leon, D. Pletcher, *J. Appl. Electrochem.* 25 (1995) 307–314.
- [32] A.A. Gallegos, D. Pletcher, *Electrochim. Acta* 44 (1999) 2483–2492.
- [33] C.A. Martínez-Huitle, E. Brillas, *Appl. Catal. B: Environ.* (2008). doi:10.1016/j.apcatb.2008.09.017.
- [34] H. Wang, X.J. Yu, D.Z. Sun, *J. Environ. Sci.* 25 (2005) 901–907.
- [35] H. Wang, X.J. Yu, D.Z. Sun, *Chin. Chem. Lett.* 16 (2005) 1129–1132.
- [36] H. Wang, J.L. Wang, *Appl. Catal. B: Environ.* 77 (2007) 58–65.
- [37] H. Wang, J.L. Wang, *Electrochim. Acta* 53 (2008) 6402–6409.
- [38] C.Y. Cui, X. Quan, S. Chen, H.M. Zhao, *Sep. Purif. Technol.* 47 (2005) 73–79.
- [39] G. Chen, Z.Y. Wang, T. Yang, D.D. Huang, D.G. Xia, *J. Phys. Chem. B* 110 (2006) 4863–4868.
- [40] A.M. Venezia, L.F. Liotta, G. Deganello, Z. Schay, D. Horváth, L. Gucci, *Appl. Catal. A: Gen.* 211 (2001) 167–174.
- [41] P. Canizares, J.A. Domingues, M.A. Rodrigo, J. Villasenor, J. Rogdriguez, *Ind. Eng. Chem. Res.* 38 (1999) 3779–3785.
- [42] I. Sirés, J.A. Garrido, R.M. Rodríguez, E. Brillas, N. Oturan, M.A. Oturan, *Appl. Catal. B: Environ.* 72 (2007) 382–394.
- [43] Y. Yasman, V. Bulatov, I. Rabin, M. Binetti, I. Schechter, *Ultrason. Sonochem.* 13 (2006) 271–277.
- [44] E. Brillas, B. Boye, M.M. Dieng, *J. Electrochem. Soc.* 150 (2003) E148–E154.
- [45] M. Pimentel, N. Oturan, M. Dezotti, M.A. Oturan, *Appl. Catal. B: Environ.* 83 (2008) 140–149.
- [46] M.E. Makgae, M.J. Klink, A.M. Crouch, *Appl. Catal. B: Environ.* 84 (2008) 659–666.